Theoretical Kinetic Study of the Unimolecular Keto - Enol Tautomerism Propen-2-ol $\leftrightarrow$ Acetone. Pressure effects and Implications in the Pyrolysis of tert- and 2-butanol

E. Grajales-González, M. Monge-Palacios, S. Mani Sarathy**

King Abdullah University of Science and Technology, Clean Combustion Research Center,
Thuwal, Saudi Arabia

ABSTRACT

The need for renewable and cleaner sources of energy has made biofuels an interesting alternative to fossil fuels, especially in the case of butanol isomers, with its favorable blend properties and low hygroscopicity. Although C₄ alcohols are prospective fuels, some key reactions governing their pyrolysis and combustion have not been adequately studied, leading to incomplete kinetic models. Enols are important intermediates in the combustion of C₄ alcohols, as well as in atmospheric processes. Butanol reactions kinetics is poorly understood. Specifically, the unimolecular tautomerism of propen-2-ol $\leftrightarrow$ acetone, which is included in butanol combustion kinetic models, is assigned rate parameters based on the tautomerism vinyl alcohol $\leftrightarrow$ acetaldehyde as an analogy. In an attempt to update current kinetic models for tert- and 2-butanol, a theoretical kinetic study of the titled reaction was carried out by means of CCSD(T,FULL)/aug-cc-pVTZ//CCSD(T)/6-31+G(d,p) *ab initio* calculations, with multistructural torsional anharmonicity and variational transition state theory considerations in a wide temperature and pressure range (200 K – 3000 K, 0.1 kPa – 10⁸ kPa).

Results differ from vinyl alcohol $\leftrightarrow$ acetaldehyde analogue reactions, which shows lower rate constant values. It was observed that decreasing pressure leads to a decrease in rate constants, describing the expected falloff behavior. Tunneling turned out to be important, especially at low temperatures. Accordingly, pyrolysis simulations in a batch reactor for tert- and 2-butanol with computed rate constants showed important differences in comparison with previous results, such as larger acetone yield and quicker propen-2-ol consumption.

1. INTRODUCTION

The industrial revolution of the late 18th and 19th centuries disclosed the world's dependency on energy, which became fundamental to the growth of economic prosperity, living standard, and development of human society.¹ Today, increased population and rapid economic and technological growth has led to a consistent increase in energy demand worldwide,² resulting in a possible unprecedented energy consumption increment of over 50% in the next 15 years.^{3,4}

Currently, 85.5% of the energy we consume comes from fossil fuels, of which 33.3%, 28.1% and 24.1% are from oil, natural gas and coal, respectively, while only 3.2% is derived from renewable sources like biofuels.⁵ Despite its broad usage, fossil fuels have several drawbacks: They are limited in nature and they will eventually deplete completely; fossil fuels reserves are also confined to a few regions, making most countries of the world energy-dependent.³ As a result, the search for alternative clean energy sources has been of increased interest in recent years.^{1,6}

Biomass plays an important role in the framework of solving environmental and energetic dilemmas,^{7,8} since its derivatives--biogas, alcohols, seed oils and biodiesel--are environmentally unobjectionable, abundant, readily available and technically feasible.⁹ Unfortunately, present biofuel projections are based mainly upon the same feedstock as food commodities and conventional agricultural resources.⁴ Among the various alternatives, n-butanol is considered a valuable biofuel due to its less hygroscopic nature, better ignition quality and blend stability, energy density and high

cetane number;¹⁰ its production also consumes less energy in comparison with fuels like ethanol.³ Other butanol isomers, such as tert- and 2-butanol have high octane numbers and can be used to improve the antiknock quality of gasoline fuels.¹¹

The literature has produced interesting studies regarding butanol isomer combustion, among the most relevant is the work of Yasunaga et al.,¹² who investigated the pyrolysis and combustion of those isomers. These authors constructed a detailed chemical kinetic model consisting of 1,892 reactions containing 284 species, which was evaluated against experimental concentration profiles and ignition delay times. Sarathy et al.¹³ carried out an even more comprehensive kinetic study for n-, 2-, iso-, and tert-butanol, examining 2,335 reactions involving 426 species, and including detailed high- and low-temperature reaction pathways in addition to specific reaction rates for particular oxidation channels of this type of alcohols. More specific studies of each butanol isomer are also available in the literature. An example is the work on tert-butanol by Jin et al.,¹⁴ in which pyrolysis tests in flow reactors were performed. This work also accounts for the implementation of a detailed kinetic model consisting of 1,486 reactions and 209 species that satisfactorily simulates the decomposition of the alcohol over a broad range of temperatures and pressures.

From a theoretical point of view, most of the kinetic mechanisms proposed only describe high temperature conditions well. Some other chemistry, important for butanol isomers at intermediate and low temperatures, is considerably less well-established.¹⁵ Therefore, it is pertinent to analyze key reactions in order to carry out further improvements when possible. As an example, in the aforementioned paper of Sarathy et al.,¹³ the kinetic mechanism (which is used in this work) included different critical propen-2-ol production and consumption channels with rate parameters assigned from analogous reactions. According to sensitivity analysis performed by Yasunaga et al.,¹² the main consumption route for propen-2-ol is acetone production (R1), followed in much lesser extent by hydrogen addition; however, the former and all keto-enol tautomerisms used kinetic data from the theoretical study of vinyl alcohol $\leftrightarrow$ acetaldehyde system performed by Da Silva et al.¹⁶ Similarly,

Jin et al.¹⁴ assumed that rate of propen-2-ol isomerization is analogous to that of vinyl alcohol isomerization from Shao et al.¹⁷ These estimations may contribute to the deviations observed between the computed and experimental concentration profiles shown in the aforementioned works for different alcohols and their corresponding aldehyde or ketone isomers.

Acetone is a key species in the combustion and pyrolysis of tert- and 2-butanol¹² and to the best of our knowledge, the only theoretical work that involves the unimolecular propen-2-ol isomerization was performed by Elango et al.,¹⁸ who determined the stationary points and the minimum energy path (MEP) without any further kinetic study. It should be noted that enols are common intermediates in the combustion of many hydrocarbons¹⁹ as well as important in atmospheric oxidation of volatile organic compounds.²⁰

Because of the scarce data related to unimolecular propen-2-ol tautomerism, a theoretical kinetic study was carried out in this work, which considered tunneling correction and multistructural torsional anharmonicity on the reaction R1, and its reverse, -R1, with the purpose of updating the kinetic model of Sarathy et al.,¹³ and consequently improving the understanding of the oxidation and pyrolysis of butanol isomers to design more efficient and cleaner combustion processes. Closed batch reactor simulations have been also conducted in this work for the pyrolysis of tert- and 2-butanol isomers to demonstrate the importance of the titled reaction.

2. COMPUTATIONAL DETAILS

2.1. Electronic structure calculations: Characterization of the potential energy surface

The first step in our procedure was to determine the number of conformers for the reactant, saddle point and product species (conformers are defined as different configurations of a given species that can be interconverted into one another by internal rotations). Conformational analysis was performed with MSTor²¹ software version 2013, where all possible torsions were evaluated with rotations of 90°, giving an overall of 4ⁿ possible structures for each species, where *n* is the number of torsions.

To each conformer, geometry optimization, frequency determination and single point energy calculations were carried out using the CCSD(T,FULL)/aug-cc-pVTZ//CCSD(T)/6-31+G(d,p) level of theory in Gaussian09²² software. With this information, zero point energy (ZPE) corrected values, or adiabatic energies for each conformer, were computed. The minimum energy conformer of each species (henceforth called *global minima*), were used to calculate the MEP by using the GaussRate17²³ software, which is an interface between Gaussian09²² and Polyrate 2016-2A.²⁴ During an MEP mapping, energies, gradients and Hessians along the steepest descent route in isoinertial coordinates were computed, starting from the saddle point. The step size selected between the -0.70 bohr – 0.70 bohr range of the reaction coordinate was 0.04 bohr, while those for the ±0.70 bohr – ±1.15 bohr and ±1.15 bohr – ±3.00 bohr were 0.07 bohr and 0.20 bohr, respectively. The step size near the saddle point was smaller because the information in this region is critical to determine the location of the transition state under the framework of variational principles, and for an accurate description of the transmission coefficients. For the same purpose, a sufficiently broad region of the MEP was covered. The Hessian was evaluated at every fourth step.

2.2. High pressure limit rate constant calculation. Multistructural variational transition state theory

With the energy, gradient and Hessian along the MEP, it is possible to compute preliminary rate constants using Polyrate 2016-2A software.²⁴ Canonical variational transition state rate constants

(CVT) were calculated using the global minimum structures (SS), the harmonic oscillator approach (HO), and small curvature tunneling corrections (SCT), labeled as $k_{SS-HO}^{CVT/SCT}$.

To include the effect of the multiple conformers on the rate constant (known as multistructural anharmonicity (MS)), it was necessary to compute multistructural partition functions. To do so, the MSTor program was used; it calculates the conformational rovibrational multistructural partition function, including torsional anharmonicity corrections (T), as²⁵

$$Q_{con-rovib}^{X,MS-T} = \sum_{j=1}^Y Q_{rot,j} \exp(-\beta U_j) Q_j^{HO} Z_j \prod_{\tau=1}^t f_{j,\tau} \quad (1)$$

where X stands for reactant R , or saddle point $\ddagger$. The label j represents a conformation of either reactant or saddle point, with J as the total number of distinguishable structures, denoted as $j=1,2,\dots,J$. Q_{rot} is the classic approximation for the rotational partition function, β is equal to $1/k_B T$. Z_j is a factor that guaranties accurate behavior for the $Q_{con-rovib}^{X,MS-T}$ partition function at high temperatures. Finally, $f_{j,\tau}$ is an internal coordinate torsional anharmonicity function which--together with Z_j --includes the effect of the torsional anharmonicity associated with each internal coordinate $\tau = 1, 2, \dots, t$. The global minimum for reactant--or saddle point--is labeled as reference with an energy value of zero, and denoted as $U_j=U_1$. Under the scope of eq 1, the torsional space is divided into two types: nearly separable (NS) and strongly coupled (SC). The last case used Voronoi tessellation²⁵ to compute the value of local periodicities necessary to calculate the partition functions.

With the multistructural torsional rovibrational partition functions (eq 1), it was possible to evaluate the multistructural torsional anharmonicity factors to correct a single structural rate constant as

$$F^{\ddagger,MS-T} = \frac{Q_{con-rovib}^{\ddagger,MS-T}}{Q_{rovib}^{\ddagger,SS-T}} \quad (2)$$

$$F^{R,MS-T} = \frac{Q_{con-rovib}^{R,MS-T}}{Q_{rovib}^{R,SS-T}} \quad (3)$$

where $Q_{rovib}^{\ddagger,SS-T}$ and $Q_{rovib}^{R,SS-T}$ represent the single structural rovibrational partition function with torsional anharmonicity corrections of the global minimum structures of the saddle point and reactant,

respectively. Eqs 2 and 3 display the multistructural torsional anharmonicity factors of the reactant and saddle point, correspondingly. The factors in eqs 2 and 3 can be also calculated without torsional anharmonicity corrections, that is, under the harmonic oscillator approach, $F^{\neq,MS-HO}$ and $F^{R,MS-HO}$. The overall multistructural torsional anharmonicity factor for a given reaction is calculated as

$$F^{MS-T} = \frac{Q_{con-rovib}^{\neq,MS-T}}{Q_{rovib}^{\neq,SS-T}} \frac{Q_{rovib}^{R,SS-T}}{Q_{con-rovib}^{R,MS-T}} \quad (4)$$

The factor in eq 4 can be also calculated without torsional anharmonicity, F^{MS-HO} , by using $F^{\neq,MS-HO}$ and $F^{R,MS-HO}$.

Rate constants considering multistructural torsional anharmonicity are given by eq 5.

$$k_{MS-T}^{CVT/SCT} = \frac{Q_{con-rovib}^{\neq,MS-T}}{Q_{rovib}^{\neq,SS-HO}} \frac{Q_{rovib}^{R,SS-HO}}{Q_{con-rovib}^{R,MS-T}} \cdot k_{SS-HO}^{CVT/SCT} \quad (5)$$

2.3. Pressure-dependent rate constant calculations

The computation of pressure-dependent rate constants was carried out with the system-specific quantum RRK theory (SS-QRRK),²⁶ as implemented in Polyrate 2016-2A,²⁴ considering only the forward reaction (R1) (values for reverse reaction can be determined with the equilibrium constant). This code has been proven to give results comparable with values computed by MS- μ VT²⁷ theory. First, values of $k_{MS-T}^{CVT/SCT}$ were fitted to the form of eq 4 shown in Bao et al.²⁷ for exothermic reactions, which in a second step gives the parameters n , E and T_0 necessary to compute the Tolman activation energy E_a , and the Arrhenius frequency factor A^∞ that are used by the SS-QRRK^{27,28} theory. This approach is based on the energy dependent Lindemann-Hinshelwood mechanism, where the computation of the de-energization rate constant uses a modified strong collision model.

The pressure range studied was from 0.1 kPa to 10^8 kPa, using nitrogen as bath gas, which is commonly used and has a de-energization temperature dependency with the form $\langle E \rangle_{down} = 200 \cdot (T/300)^{0.85} \text{ cm}^{-1}$ (determined by fitting experimental falloff curves²⁹). The other bath gas used was

argon, which dilutes 2- and tert-butanol in our pyrolysis simulations and has a de-energization value $\langle E \rangle_{down} = 400 \text{ cm}^{-1}$, as reported by Zhu and Lin.³⁰ The Lennard-Jones parameters implemented for propen-2-ol were those of n-propanol, $\sigma=4.549 \text{ \AA}$ and $\varepsilon/k_B= 576.7 \text{ K}$, which were also adopted by Zhou et al.³¹ to study propen-2-ol decomposition reactions. Nitrogen has the parametric values $\sigma=3.798 \text{ \AA}$ and $\varepsilon/k_B= 71.4 \text{ K}$, and for argon these parameters are $\sigma=3.542 \text{ \AA}$, $\varepsilon/k_B= 93.3 \text{ K}$.

2.4. Numerical pyrolysis simulations

The kinetic mechanism of Sarathy et al.¹³ for butanol isomers was updated with the computed rate constants for the reactions R1 and -R1; this model is hereafter referred to as *the updated model*. The objective was to determine the role of the calculated rate constants by comparing the predictions of the updated model to those of the former model, which describes reactions R1 and -R1 using an analogy.

Pyrolysis numerical simulations of tert- and 2-butanol, with the same initial conditions as Yasunaga et al.,¹² were performed with ANSYS CHEMKIN-PRO 18.1³² software, using a closed homogeneous batch reactor where tert- and 2-butanol had a composition of 0.01 and 0.015 mole fraction, respectively, diluted in argon. Two different types of simulations were performed; in the first one (hereafter *transient simulation*), values of concentrations of key species during the pyrolysis process were monitored at 1300 K, during 2000 μs and 2500 μs for tert- and 2-butanol, correspondingly. In the second type of simulation (*temperature-dependent simulation*), the same analysis was performed at temperatures between 1000 K and 1500 K, monitoring the concentration of key species at the end of the simulation; the goal being to analyze the effect of temperature. The simulations with tert-butanol were performed at 172.3 kPa (1.7 atm), while those with 2-butanol were at 192.5 kPa (1.9 atm).

3. RESULTS AND DISCUSSION

3.1. Conformational search and topology of the PES

Figure 1 shows optimized geometries at the CCSD(T)/6-31+G(d,p) level of the different species involved in the studied reactions. For propen-2-ol, three conformers were found; its global minimum shows the OH group pointing towards the double bond (Figure 1 (a)). The conformer shown in Figure 1 (b) has a non-superimposable mirror image (enantiomer), because the OH group is not in the plane formed by the atoms O(9)-C(1)-C(2)-C(6). Two possible saddle points have the same energy; and Figure 1 (c) shows the optimized geometry of one of the enantiomers. For acetone, a single conformer was found (Figure 1 (d)).

Figure 1. Optimized structures of the reactant, saddle point and product species at the CCSD(T)/6-31+G(d,p) level. Enantiomers of geometries in (b) and (c) are not shown.

Figure 2. (a) Adiabatic potential energy (potential energy + ZPE) profile at the CCSD(T,FULL)/aug-cc-pVTZ//CCSD(T)/6-31+G(d,p) level of theory with respect to the energy of the reactant global minimum structure. Green line represents global minimum conformers; red line corresponds to the higher energy conformers. (b) MEP (potential energy, ZPE excluded) computed at the CCSD(T)/6-31+G(d,p) level using the global minimum conformers.

Figure 2 (a) shows the adiabatic potential energy profile of the propen-2-ol $\leftrightarrow$ acetone tautomerism. The energy difference between the conformers of the reactant propen-2-ol is 1.94 kcal mol⁻¹, and the enthalpies of reaction at 0 K and 298 K are -11.38 kcal mol⁻¹ and -12.92 kcal mol⁻¹, respectively. With enthalpies of formation (at 298 K) from the NIST³³ database, an enthalpy of reaction of -10.16 was calculated, indicating that the value was close to the experimental value.

Figure 2 (b) shows the MEP computed using the CCSD(T)/6-31+G(d,p) level for the global minimum conformers of the different species. Propen-2-ol is taken as the classic energy reference point (without the zero point energy correction). Note that the kinetic study was based on a scaled MEP aimed to reproduce the CCSD(T,FULL)/aug-cc-pVTZ//CCSD(T)/6-31+G(d,p) single point energies. At this level, the energy barrier of the reaction is 57.7 kcal mol⁻¹, 3.5 kcal mol⁻¹ higher than the barrier obtained by Elango et al.¹⁸ using the lower MP2/cc-pVDZ level of theory. As expected for

a gas phase non-catalyzed keto-enol tautomerism, a large barrier height was obtained.³⁴ The energy of reaction was $-11.1 \text{ kcal mol}^{-1}$, which was also different from the value obtained in the referenced work,¹⁸ $-14.5 \text{ kcal mol}^{-1}$.

3.2. Rate constants determination

With the data calculated along the MEP, the value of the transmission coefficients was obtained; it has the temperature dependence shown in Figure 3. As expected for a hydrogen shift reaction with a large barrier, tunneling was highly pronounced in both R1 and $-R1$ reactions, with an order of magnitude of around 10^9 at 298 K.

Figure 4 (a) shows the values of the multistructural anharmonicity factor for propen-2-ol, with and without torsional anharmonicity, F^{MS-T} and F^{MS-LH} , respectively. The former starts with a value of one at low temperature and tends to a value of two at higher temperatures. The latter begins with the same unity value, but at higher temperatures it tends to three--the total number of structures found for this specie. Thus, the torsional anharmonicity correction is important in the reactant propen-2-ol.

Figure 3. Transmission coefficients computed with the SCT method for reactions R1 (black line) and $-R1$ (red line).

The saddle point has an anharmonicity factor of two over the studied temperature range, as a result of its two equivalent conformers. Finally, the anharmonicity factor of acetone--which has just one structure--always takes a value of unity.

Figure 4. (a) Anharmonicity factor for propen-2-ol (b) anharmonicity factors for reactions R1 (f subscript), and -R1 (r subscript).

The total factor for the reaction (eq 4) was the result of the factor of each of the species involved in the reaction. In Figure 4 (b) the effect of the torsional anharmonicity for the reaction R1 is shown to be important and will affect the value of the rate constant, especially at high temperatures. The anharmonicity factor for the reaction -R1 is two in the entire temperature range, with no effect from the torsional anharmonicity ($F^{MS-T} = F^{MS-LH}$).

Figure 5. High-pressure rate constants as function of temperature. Computed values are black and red lines for reactions R1 and $-R1$, respectively. Green and blue lines are forward and reverse rate constants, respectively, determined by Da Silva et al.¹⁶ for the vinyl alcohol $\leftrightarrow$ acetaldehyde reaction used as analogy in previous models.

Figure 5 shows the fitting of the final calculated high-pressure limit rate constants (eq 5) for the reactions R1 (black line) and $-R1$ (red line). The curvature of the plots is due to the large values of the transmission coefficients. It is also important to note that R1 reaction is much quicker than $-R1$ in the entire temperature range, favoring the keto form.

The variational effect for reactions R1 and $-R1$ proved to be negligible because the shift of the transition state with respect to the saddle point was negligible, as is typical for a sharp barrier and a tight saddle point. The displacement on the reaction coordinate of the transition state with respect to the saddle point was only of 0.0019 Å and 0.0024 Å at 200 K and 3000 K, respectively. As a consequence, the forward rate constants with and without variational effects are quite similar: $6.24 \cdot 10^{-47} \text{ s}^{-1}$ and $6.23 \cdot 10^{-47} \text{ s}^{-1}$ at 200 K, and $4.55 \cdot 10^9 \text{ s}^{-1}$ and $4.56 \cdot 10^9 \text{ s}^{-1}$ at 3000 K for the transition state theory (TST) and variational transition state theory (VTST), respectively. The reverse reaction shows a similar trend. Once the Hessians along the reaction path have been computed, in order to accurately estimate tunneling effect, VTST rate constants can be computed with Polyrate without additional

computational cost; therefore, we opted for using them due to the more rigorous theoretical approach they are based on.

The high-pressure rate constants in the entire temperature range (200 K – 3000 K) were fitted to the following equation³⁵

$$k = A \left(\frac{T}{300} \right)^n \exp \left(- \frac{E(T - T_0)}{R(T^2 + T_0^2)} \right) \quad (6)$$

However, since CHEMKIN software must be provided with kinetic information by means of a three-parameter Arrhenius equation (also known as modified Arrhenius equation),

$$k = A T^n \exp(-E/RT) \quad (7)$$

the rate constants over the temperature range 600 K – 3000 K (the temperature range in this study) were also fitted to eq 7 as follows:

$$k_{f,MS-T}^{CVT/SCT} = 2.569 \cdot 10^{12} \left(\frac{T}{300} \right)^{0.613} \exp \left(- \frac{41.617(T - 318.837)}{R(T^2 + 318.837^2)} \right) \quad (8)$$

$$k_{r,MS-T}^{CVT/SCT} = 5.067 \times 10^{-4} \left(\frac{T}{300} \right)^{5.234} \exp \left(- \frac{44.689(T - 250.285)}{R(T^2 + 250.285^2)} \right) \quad (9)$$

$$k_{f,MS-T}^{CVT/SCT} = 1.730 \cdot 10^5 T^{2.302} \exp \left(- \frac{46.989}{RT} \right) \quad (10)$$

$$k_{r,MS-T}^{CVT/SCT} = 1.564 \times 10^{-10} T^{3.614} \exp \left(- \frac{59.679}{RT} \right) \quad (11)$$

where R and T are the ideal gas constant and temperature with units of kcal mol⁻¹ K⁻¹ and K, respectively. The units of the fitting parameters A , T_0 and E are s⁻¹, K and kcal mol⁻¹, respectively.

Figure 5 also includes rate constants determined by Da Silva et al.¹⁶ for the reaction vinyl alcohol $\leftrightarrow$ acetaldehyde, which were used as analogy to the studied reaction by Sarathy et al.¹³ The most significant discrepancies are present at low temperatures. At 298 K, deviations of about 10 and 2 orders of magnitude were obtained for R1 and –R1 reactions, respectively, mainly due to the effect of tunneling in the propen-2-ol $\leftrightarrow$ acetone tautomerism, which at that temperature has values of an order of magnitude of 9 and 8 for R1 and –R1, respectively. It is important to bear in mind that differences in the rate constants may also arise from more subtle aspects, such as the different nature

of the systems, leading to different partition functions and barrier heights, which are hard to resolve in detail.

Figure 6. Equilibrium constant for the propen-2-ol $\leftrightarrow$ acetone tautomerism.

Shao et al.¹⁷ also computed the parameters of eq 7 for the forward reaction of the vinyl alcohol $\leftrightarrow$ acetaldehyde tautomerism at 100 atm, obtaining rate constants that differ by around 40 and 3 orders of magnitude at 298 K and 3000 K, respectively. As in the case of Da Silva et al.,¹⁶ they also determined kinetic parameters that differed greatly from those calculated in this study.

Figure 6 shows the equilibrium constant for the reaction under study, calculated with the high-pressure forward and reverse rate constants. As expected for exothermic reactions, the value of this thermodynamic property decreases with an increase in temperature. Nonetheless, it is noteworthy that even at high temperatures, the value of this constant is still considerable--of the order of 10^{11} . Thus, the keto form is thermodynamically favored over the studied temperature range.

The pressure-dependent rate constants for reaction R1 in nitrogen are presented in Figure 7 by both, the relation of the rate constant obtained at pressure p to that at the high-pressure limit (it is the same figure for the reverse reaction) as function of pressure (a), and considering the sole rate constants at different pressures as function of temperature (b).

Figure 7. Pressure-dependent rate constants. (a) Falloff curves for reaction R1 as the relation of the rate constant computed at pressure p to that computed at the high pressure limit, $k(\infty)$, that is $k_{MS-T}^{CVT/SCT}$, as function of pressure. (b) Rate constants as function of pressure and temperature for reaction R1.

As expected for a unimolecular isomerization, the rate constant decreases as the pressure decreases due to the lack of collisions to repopulate the thermally activated reactant. This decrease is more pronounced at high temperatures. As shown in Figure 7 (a), below 600 K the rate constants are virtually pressure-independent with values of $\log_{10}[k(p)/k(\infty)]$ of $-2.47 \cdot 10^{-3}$ and $-8.92 \cdot 10^{-4}$ at 10^8 and 0.1 kPa, respectively. At temperatures higher than 600 K the falloff of the unimolecular isomerization rate coefficients becomes relevant. For instance, at 3000 K the rate constants at 0.1, 1.0 and 10.0 kPa decrease with respect to those at the high-pressure limit by a factor of $1.27 \cdot 10^{-7}$, $1.26 \cdot 10^{-6}$ and $1.24 \cdot 10^{-5}$, respectively. At that high temperature the value of the rate constant goes from $6.06 \cdot 10^9 \text{ s}^{-1}$ at the high-pressure limit to $7.71 \cdot 10^2 \text{ s}^{-1}$ at 0.1 kPa, with the differences shrinking as we go lower in temperature and higher in pressure.

Table 1 shows the parameters of the modified Arrhenius equation (Eq 7) resulting from the fitting of the rate constants at pressures ranging from 0.101325 to 101325 kPa using Argon as bath gas (the diluting gas used in our simulations), which were used to carry out the pyrolysis simulations, together with those obtained for the rates using N_2 (plotted in Figure 7). These equations were fitted in the temperature range of 600 K – 2000 K.

Table 1. Fitting parameters of the modified Arrhenius equation at different pressures for the reactions R1 and -R1 using Ar and N₂ as bath gasses.

Pressure (kPa)	Bath Gas	Forward			Reverse		
		A (s ⁻¹)	n ^a	E (kcal mol ⁻¹)	A (s ⁻¹)	n ^a	E (kcal mol ⁻¹)
0.101325	Ar	2.054×10^{76}	-19.453	76.335	1.007×10^{61}	-18.063	88.876
	N ₂	1.031×10^{63}	-15.386	70.809	5.054×10^{47}	-13.997	83.350
1.01325	Ar	2.179×10^{69}	-17.081	75.399	1.068×10^{54}	-15.691	87.940
	N ₂	9.530×10^{54}	-12.734	69.070	4.672×10^{39}	-11.345	81.611
10.1325	Ar	4.258×10^{56}	-13.105	70.899	2.087×10^{41}	-11.715	83.440
	N ₂	9.068×10^{41}	-8.702	64.101	4.445×10^{26}	-7.312	76.642
101.325	Ar	1.889×10^{40}	-8.142	63.816	9.259×10^{24}	-6.752	76.357
	N ₂	6.957×10^{26}	-4.138	57.344	3.411×10^{11}	-2.748	69.885
1013.25	Ar	9.831×10^{23}	-3.270	56.141	4.819×10^{08}	-1.880	68.682
	N ₂	6.740×10^{13}	-0.257	51.103	3.304×10^{-02}	1.133	63.644
10132.5	Ar	4.321×10^{11}	0.398	50.059	2.118×10^{-04}	1.788	62.600
	N ₂	1.094×10^{06}	2.052	47.228	5.361×10^{-10}	3.442	59.769
101325	Ar	1.207×10^{05}	2.335	46.752	5.917×10^{-11}	3.725	59.293
	N ₂	1.682×10^{03}	2.883	45.802	8.246×10^{-13}	4.272	58.343

^a Parameter “n” is unitless.

3.3. Role of the unimolecular tautomerism propen-2-ol ↔ acetone in the pyrolysis of tert- and 2-butanol

This section compares the performance of the original kinetic model of Sarathy et al.¹³ and the updated model, to clarify the role of the studied reactions in the pyrolysis of tert- and 2-butanol isomers.

3.3.1. *tert*-Butanol.

Figure 8 shows the results of pyrolysis simulations for *tert*-butanol ($t\text{-C}_4\text{H}_9\text{OH}$) at 172.25 kPa (1.7 atm). Solid lines correspond to results obtained with the updated model; dashed lines correspond to those obtained in the model of Sarathy et al.¹³ In Figure 8 (a) it can be seen that the new set of rate constants predicts a larger yield of acetone (CH_3COCH_3) and a faster consumption of propen-2-ol ($i\text{-C}_3\text{H}_5\text{OH}$) in the transient simulations (right y-axis). No differences were observed in the concentration profile of *tert*-butanol (left y-axis) between the two kinetic models used in the simulations.

As for the temperature-dependent simulation, both models predict the same concentration for methane (CH_4) and *tert*-butanol throughout the entire temperature range (Figure 8 (b), left y-axis). An interesting behavior observed with the updated model was the lower yield of acetaldehyde (CH_3CHO) between 1200 and 1500 K (Figure 8 (b), right y-axis), whose production competes with the tautomerism propen-2-ol $\leftrightarrow$ acetone, as shown in Yasunaga et al.,¹² indicating a major role of the studied isomerization in the updated model. Figure 8 (c) shows a larger yield of acetone with the updated model at temperatures below 1400 K, as well as a slightly larger yield of carbon monoxide (CO) at any temperature. However, no notable differences were observed in either model for the isobutylene ($i\text{-C}_4\text{H}_8$) and propene (C_3H_6) species.

Figure 8. Species concentration profiles in pyrolysis of tert-butanol. Solid and dashed lines are updated and Sarathy et al.¹³ models, respectively. (a) Concentration profile of propen-2-ol, acetone and tert-butanol as function of time. (b) Concentration profile of tert-butanol, methane and acetaldehyde as function of temperature. (c) Concentration profile of acetone, carbon monoxide, isobutylene and propene as function of temperature.

3.3.2. 2-Butanol.

This alcohol presents concentration trends similar in the transient simulation to tert-butanol, as illustrated in Figure 9 (a). However, the differences between both kinetic models are more remarkable.

Figure 9. Species concentration profiles in pyrolysis of 2-butanol. Solid and dashed lines correspond to updated and Sarathy et al.¹³ models, respectively (a) Concentration profile of propen-2-ol, acetone and 2-butanol as function of time. (b) Concentration profile of acetone, propen-2-ol, 2-butanol and acetaldehyde as function of temperature.

In the updated model, the increase in the concentration of acetone (Figure 9 (a), right y-axis) is more pronounced, and the decrease of propen-2-ol profile (Figure 9 (a), right y-axis) is also more noticeable in comparison with its corresponding graph for tert-butanol in Figure 8 (a). In general, the concentration of propen-2-ol in the pyrolysis of 2-butanol ($\text{s-C}_4\text{H}_9\text{OH}$) is higher than in the pyrolysis of tert-butanol.

Concentration profiles in temperature-dependent simulations of species of interest are also shown in Figure 9 (b). With the updated model, the yield of acetone is larger, while that of propen-2-ol is lower, over almost the entire range of temperatures studied. On the other hand, 2-butanol does not show a notable change in its concentration profile. One remarkable fact was the decrease in the concentration of acetaldehyde, explained by the preference of the new model to take the propen-2-ol $\rightarrow$ acetone channel instead of the propen-2-ol $\rightarrow$ vinyl alcohol $\rightarrow$ acetaldehyde path, carried out by methyl elimination and keto - enol tautomerism.

4. CONCLUSIONS

A theoretical kinetic study was performed on the unimolecular tautomerism propen-2-ol $\leftrightarrow$ acetone by means of electronic structure calculations at the CCSD(T,FULL)/aug-cc-pVTZ//CCSD(T)/6-31+G(d,p) *ab initio* level, and multistructural variational transition state theory treatment (thus including the effect of multiple conformers) with torsional anharmonicity. Pressure effects were also considered to obtain low pressure rate constants. For propen-2-ol, saddle point, and acetone species, three, two and one conformers, respectively, were found and included in our forward and reverse rate constants calculations.

It was also found that the tunneling effect plays an important role in the studied reactions, especially at low temperatures where the value of the transmission coefficients achieves an order of magnitude of 10^9 at 298 K. Torsional anharmonicity proved to be important for propen-2-ol, also affecting the value of the rate constant of the forward reaction, for which the free rotor approximation is required- especially at high temperatures. The values of the rate constants of the forward reaction were larger than those of the reverse reaction for more than 10 orders of magnitude, resulting in a large equilibrium constant and favoring the keto form. On the other hand, pressure-dependent rate constants showed the falloff trend over 600 K and below 10^8 kPa.

Current kinetic models use the reaction vinyl alcohol $\leftrightarrow$ acetaldehyde as analogy to the studied tautomerism, thus failing to accurately reproduce the concentration profiles of propen-2-ol and acetone, among other species. This is the case of the kinetic model by Sarathy et al.,¹³ updated in this work with the calculated rate constants. The objective was to compare the effect of the new sets of rate constants in the pyrolysis of tert- and 2-butanol isomers by performing simulations in a closed homogeneous batch reactor and analyzing concentration profiles of key species at transient state and as a function of temperature.

Because of the larger rate constants obtained in this work compared to those used as analogy, the updated model predicts a faster consumption of propen-2-ol and a larger production of acetone than the former model. Carbon monoxide in tert-butanol and acetaldehyde in tert- and 2-butanol showed an increase and decrease in concentration, respectively, with the updated model, a fact that is explained by considering reaction channels described elsewhere.¹² Because of these relevant differences, it is convenient to study other sensitive keto-enol tautomerisms for propen-2-ol (i.e., radical assisted channels) to avoid the use of analogies and improve the predictions of the concentration profiles of all related species, as well as other important properties in combustion and pyrolysis processes.

These rate constants are useful to update current kinetic models for butanol isomers, improving their performance and clarifying the combustion and pyrolysis processes of this important biofuel. In addition, the rate constants presented here can be used to better understand enol chemistry in atmospheric systems.

AUTHOR INFORMATION

Corresponding Authors

Manuel Monge-Palacios, PhD <manuel.mongepalacios@kaust.edu.sa>

S. Mani Sarathy, PhD <mani.sarathy@kaust.edu.sa>

4700 King Abdullah University of Science and Technology

Al Kindi Building 5

Thuwal, Saudi Arabia 23955

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